$ A/Reissue

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July 16, 1997

Asst. Commissioner for Patents
Washington, D.C. 20231

Re: Continuation of U.S. Serial No. 08/324,260
Atty. Docket: HOE 90/F 333C (139*2349)
Applicant(s): Andreas Winter et al
Examiner: David Wu - Art Unit: 1505

DEMAND FOR DIVISION OF REISSUE APPLICATION UNDER 37 CFR §1.177

Sir:

This is a request for filing a continuation application under Rule 60 of pending application Serial No. 08/324,260 filed October 17, 1994, in the name(s) Andreas Winter, Martin Antberg, Walter Spaleck, Jurgen Rohrmann and Volker Dolle.

Enclosed is a copy of the prior application as filed originally and an affidavit verifying it as a true copy. Also enclosed are copies of the Reissue Declaration and other reissue papers submitted in Serial No. 08/324,260.

A check in payment of the filing fee, calculated as follows is attached.

Basic fee	$770.00
Total number of claims in excess of 20, times $22	22.00
Number of independent claims in excess of 3, times $80	_____
TOTAL FILING FEE	$792.00

Attached hereto is a proposed Preliminary Amendment to the specification and claims of the requested continuation application. It is respectfully requested that the filing fee be calculated after entry of the Preliminary Amendment. The fee for the additional claim is enclosed.

The prior application is assigned to Hoechst Aktiengesellschaft, a corporation of the Federal Republic of Germany, in an assignment recorded Reel 5910, Frame 753. Please apply the assignment to this continuing case.

Please charge any additional fees connected with filing of the application or its prosecution to Deposit Account No. 03-2775. This is a general authorization under 37 CFR 1.25(b), except that no automatic debit of the issue fee upon issuance is authorized. This letter is being sent in triplicate.

Kindly send us the official filing receipt.

Respectfully submitted,

CONNOLLY & HUTZ

By _____
Thomas M. Meshbesher
Reg. No. 25,083
Tel. (302) 658-9141

TMM/dcp (8413)

"Express Mail" No.: EI 458069705 US Date: July 17, 1997

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Asst. Commissioner for Patents, Washington, D.C. 20231

THOMAS M. MESHBESHER
(Typed or printed name) of person mailing paper or fee)

_____
(Signature of person mailing paper or fee)

Docket HOE 90/F 333B (139*1590)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

ANDREAS WINTER ET AL	:	
REISSUE OF U.S. PATENT 5,276,208	:	PARENT BEFORE
SERIAL NO:	:	ART UNIT: 1505
FILED:	:	EXAMINER: WU
FOR: METALLOCENES CONTAINING LIGANDS OF 2-SUBSTITUTED INDENYL DERIVATIVES, PROCESS FOR THEIR PREPARATION AND THEIR USE AS CATALYSTS	:	

Hon. Commissioner of Patents and Trademarks
Washington, D.C. 20231

"Express Mail" No.: EF 183978800 Date: October 17, 1994

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231

Diane C. Pickering
(Typed or printed name of mailing paper or fee)

Diane C. Pickering
(Signature of person mailing paper)

REISSUE APPLICATION TRANSMITTAL

Sir:

Transmitted herewith is the application for reissue of U.S. Patent No. 5,276,208, issued on January 4, 1994.

Inventor(s): Andreas Winter, Martin Antberg, Walter Spaleck, Jürgen Rohrmann and Volker Dolle.

Title: METALLOCENES CONTAINING LIGANDS OF 2-SUBSTITUTED IDENYL DERIVATIVES, PROCESS FOR THEIR PREPARATION, AND THEIR USE AS CATALYSTS.

Enclosed (or noted below) are:

1. ☒ Specification and Claims.

2. ☐ Declaration and power of attorney by Inventors.

3. ☐ Offer by the Assignee to surrender the original letters patent in accordance with 37 CFR 1.178.

4. ☐ Assent of the Assignee to reissue.

5. ☒ Order for an abstract of title (37 CFR 1.171).

6. ☐ Information Disclosure Statement/PTO Form 1449

7. ☐ Priority of application P 40 35 884.4, filed on November 12, 1990 in the Federal Republic of Germany is claimed under 35 U.S.C. 119. The certified copy has been filed in prior application serial no. 07/789,361, filed on November 8, 1991.

8. Fee Calculation:

CLAIMS	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
	TOTAL CLAIMS	18 - 20 =	none	X $22.00=	$ 0.00
	INDEPENDENT CLAIMS	3 - 3 =	none	X $76.00=	0.00
	MULTIPLE DEPENDENT CLAIMS (if applicable)			+ $230.00=	
				BASIC FEE	+ 730.00
			Total of above Calculations =		730.00
	Reduction by 50% for filing by small entity 37 CFR 1.9, 1.27, 1.28. Verified Statement enclosed.				
				TOTAL =	730.00

9. ☐ Method of Payment of Fees: undersigned's check (enclosed).

10. ☒ Preliminary Communication (and attached copy of pending Request for Certificate of Correction).

11. ☒ The original patent, no. 5,276,208, was issued without a Drawing.

12. ☐ Letter requesting transfer of Drawing under 37 CFR §1.174.

13. ☒ Authorization To Charge Additional Fees:
The Commissioner is hereby authorized to charge any additional fees required by this paper and the accompanying application to Account No. 03-2775. See enclosed "General Authorization", submitted in triplicate.

Respectfully Submitted,

TMM / [signature] 30,962

Thomas M. Meshbesher
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CONNOLLY AND HUTZ
1220 Market Street
Wilmington, Delaware 19899
Attorney of Record

92463

HOE 90/F 333C (139*2349)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

ANDREAS WINTER ET AL	:	
REISSUE OF U.S. PAT. 5,276,208 Demand For Division (37 CFR §1.177) Of SERIAL NO: 08/324,260	:	Parent Before: ART UNIT: 1505
FILED: OCTOBER 17, 1994	:	EXAMINER: Wu
FOR: METALLOCENES CONTAINING LIGANDS OF 2-SUBSTITUTED INDENYL DERIVATIVES, PROCESS FOR THEIR PREPARATION, AND THEIR USE AS CATALYSTS	:	

Asst. Commissioner for Patents
Washington, D.C. 20231

"Express Mail" No.: EI 458069705 US Date: July 17, 1997

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231

THOMAS M. MESHBESHER
(Typed or printed name) of person mailing paper or fee)

(Signature of person mailing paper or fee)

PRELIMINARY AMENDMENT

Sir:

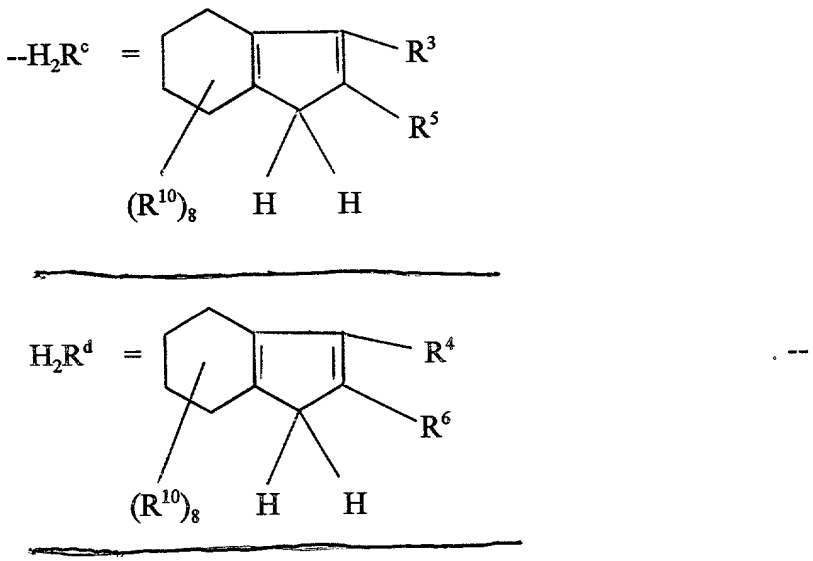
Preliminary to examination, please enter the following amendment.

On page (column) 1, below the descriptive title, please insert the following as the first paragraph of the application:

--This application is a voluntary division under 37 CFR 1.177 of copending reissue application Serial No. 08/324,260, filed October 17, 1994.--

In the Specification

On page (column) 7, second and third lines (second and third structural formulas, for "H_2R^c" and "H_2R^d"), please delete the entire two lines and insert the following therefor:



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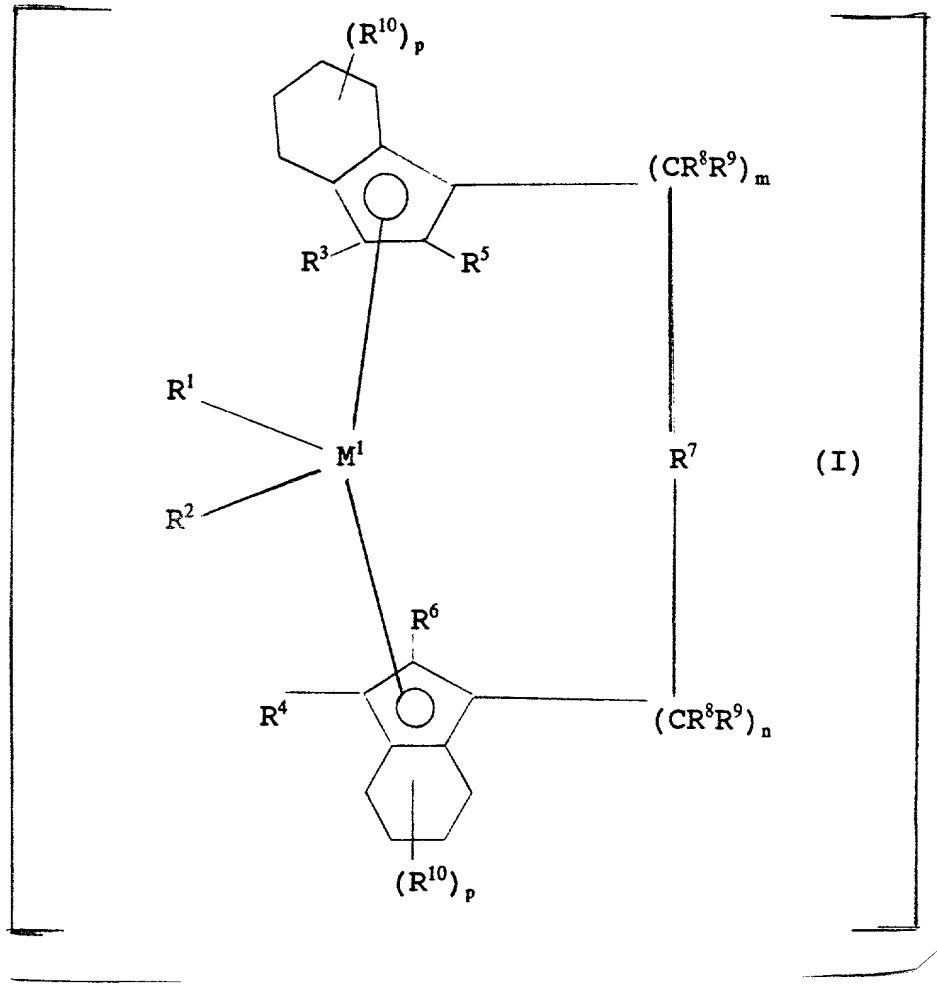
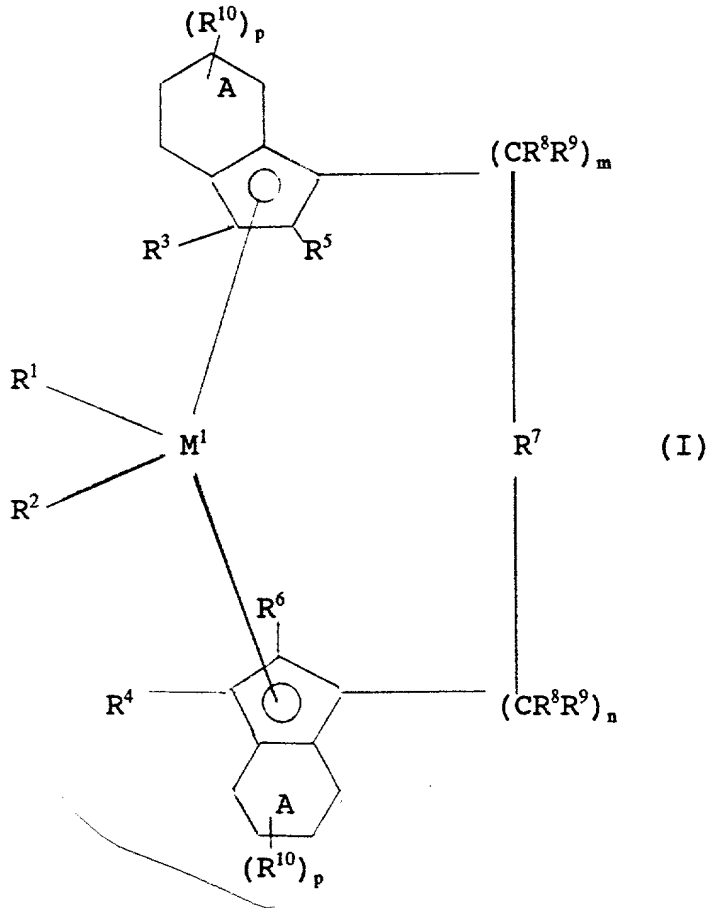
In the Claims

Please amend claim 1 on pages 16 and 17 (columns 16 and 17) of the instant specification as set forth below:

--1. (Twice amended) A compound of the formula I [for preparing essentially isotactic olefin polymers]


(R10)p
(CR8R9)m
R3
R5
R1
M1
R7
(I)
R2
R6
R4
(CR8R9)n
(R10)p



in which

M^1 is a metal from group IVb, Vb or VIb of the Periodic Table

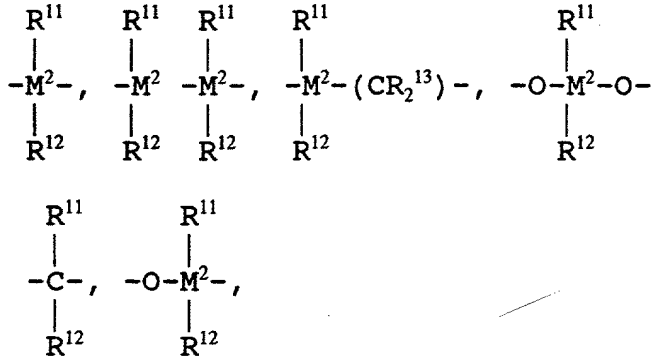
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl

group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, [a halogen atom,] a C_1-C_{10}-alkyl group, which is optionally halogenated, a C_6-C_{10}-aryl group, an $-NR_2^{15}$, $-SR^{15}$, $-OSiR_3^{15}$, $-SiR_3^{15}$ or $-PR_2^{15}$ radical in which R^{15} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and are as defined for R^3 and R^4, with the proviso that R^5 and R^6 are not hydrogen,

R^7 is



$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $=P(O)R^{11}$,

where

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_6-C_{10}-fluoroaryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or a pair of substituents R^{11} and R^{12}-- or R^{11} and R^{13} in each case with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and are as defined for R^{11}

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2, [and]

the radicals R^{10} are identical or different and are as defined for R^{11}, R^{12} and R^{13}.

rings A are saturated or aromatic,

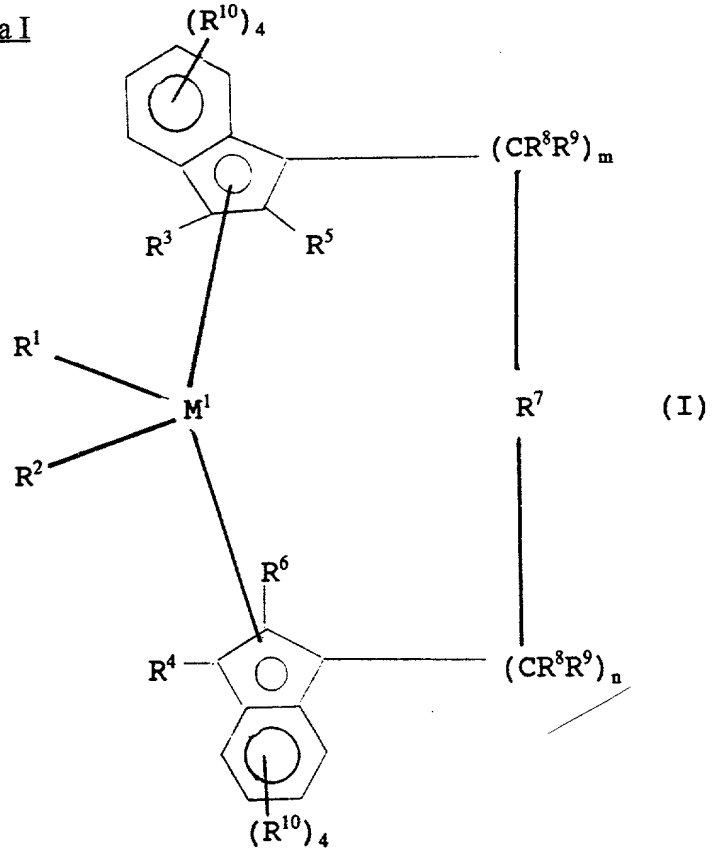
p is 8, when rings A are saturated, and

p is 4, when rings A are aromatic.--

Please cancel the duplicate "claim 1" on page 19 of the application (following claim 15).

Please cancel claims 16 to 18, and insert the following new claims therefor.

19. A compound of the formula I



in which

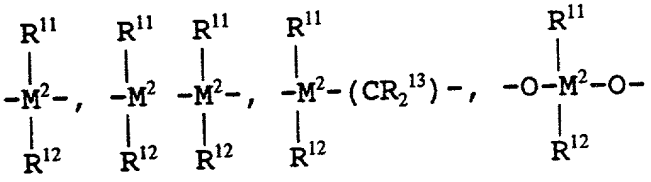
M^1 is a metal from group IVb, Vb or VIb of the Periodic Table,

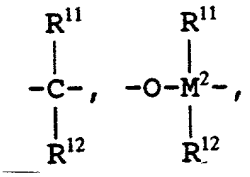
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, which is optionally halogenated, a C_6-C_{10}-aryl group, an $-NR_2^{15}$, $-SR^{15}$, $-OSiR_3^{15}$, $-SiR_3^{15}$ or $-PR_2^{15}$ radical in which R^{15} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and are as defined for R^3 and R^4, with the proviso that R^5 and R^6 are not both hydrogen,

R^7 is





=BR^{11}, =AlR^{11}, -Ge-, -Sn-, -O-, -S-, =SO, =SO_2, =NR^{11}, =CO, =PR^{11} or =$P(O)R^{11}$,

where

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or a pair of substituents R^{11} and R^{12} --or R^{11} and R^{13}, in each case with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and are as defined for R^{11},

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2,

the radicals R^{10} are the same or different and are as defined for R^{11}, R^{12} and R^{13}.

20. A compound as claimed in claim 19, wherein:

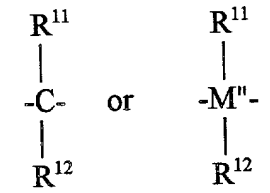
M^1 is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

R^1 and R^2 are identical or different and are methyl or halogen,

R^3 and R^4 are hydrogen,

R^5 and R^6 are identical or different and are methyl, ethyl, or trifluoromethyl,

R^7 is a radical of the formula



where M" is silicon or germanium, and

R^8 and R^9 are identical or different and are hydrogen or C_1-C_{10}-alkyl.--

Please cancel claims 16 to 18, and insert the following new claims therefor.

21. A catalyst composition comprising the combination comprising a compound of claim 19 and a cocatalyst.

22. A catalyst composition comprising the combination comprising a compound of claim 19 and an aluminoxane.

23. A process for polymerizing an olefin monomer, comprising the step of carrying out the polymerization in the presence of a catalyst composition of claim 21.

24. A process for polymerizing an olefin monomer, comprising the step of carrying out the polymerization in the presence of a catalyst composition of claim 22.--

REMARKS

Upon entry of this Preliminary Amendment, the claims of this voluntary division of the reissue application Serial No. 08/324,260 will be original claim 1 (as amended herein), original claims 2 to 15, and new claims 19 to 24. Claims 1-15, 19 and 20 are all directed to metallocene compounds. New claims 21 and 22 are directed to catalyst compositions in which the metallocene is combined with a cocatalyst (which general type of combination is considered in the art to form a new chemical compound from its metallocene and cocatalyst components). New claims 23 and 24 are directed to processes of polymerization utilizing the catalyst of claim 21 or 22. With regard to the formation of a new chemical compound from a metallocene component and a cocatalyst component, see the discussion of "preactivat[ion]" on page (column) 13, the first 14 lines under the heading "Example 1". The support for the

amendment to claim 1 and new claims 19 and 20 has been pointed out in detail in reissue application Serial No. 08/ 324,260. New claims 21 to 24 are based upon the instant disclosure, as explained in more detail below.

New claims 21 and 22:	column 7, line 5 to column 8, line 56; see also instant Examples 1 to 6 in column 13, column 14, and column 15, lines 1 and 2.
New claims 23 and 24:	column 9, line 7 to antepenultimate paragraph of the column; see also instant Examples 1 to 6 (columns 13 to 15).

The fee for the additional claim in excess of 20 is enclosed. It will be noted that the number of independent claims has not been increased beyond 3. If the undersigned has miscalculated or inadvertently omitted the required fee, the Commissioner's attention is respectfully directed to the "general authorization" to debit the undersigned's Deposit Account No. 03-2775 (copied from the parent case), submitted herewith.

It is believed that the corrections to the instant specification in column 7, second and third lines, will be self-explanatory. (Saturated six-member rings were intended for "H_2R^c" and "H_2R^d".) These changes in column 7 are actually the correction of printing errors which the applicants inadvertently failed to include in their request for a Certificate of Correction. A copy page 10 of the original specification which matured into U.S. Patent 5,276,208 is

attached to this Supplemental Amendment as Exhibit A.

Prompt, favorable action is solicited.

Respectfully submitted,

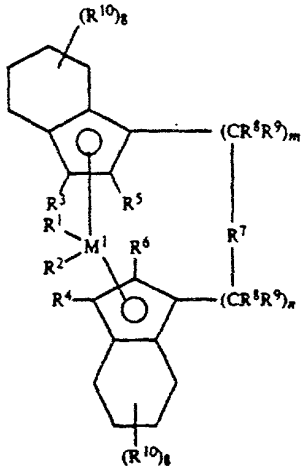
CONNOLLY & HUTZ

By _____
Thomas M. Meshbesher
Reg. No. 25,083
Tel. (302) 658-9141

TMM/dcp (8457)

[57] ABSTRACT

The novel metallocenes of the formula I



(I)

in which, preferably, M^1 is Zr or Hf, R^1 and R^2 are alkyl or halogen, R^3 and R^4 are hydrogen, R^5 and R^6 are alkyl or haloalkyl, $-(CR^8R^9)_m-R^7-(CR^8R^9)_n-$ is a single- or multi-membered chain in which R^7 may also be a (substituted) hetero atom, m+n is zero or 1, and R^{10} is hydrogen, form, together with aluminoxanes as cocatalysts, a very effective catalyst system for the preparation of polyolefins of high stereospecificity and high melting point.

15 Claims, No Drawings

METALLOCENES CONTAINING LIGANDS OF 2-SUBSTITUTED IDENYL DERIVATIVES, PROCESS FOR THEIR PREPARATION, AND THEIR USE AS CATALYSTS

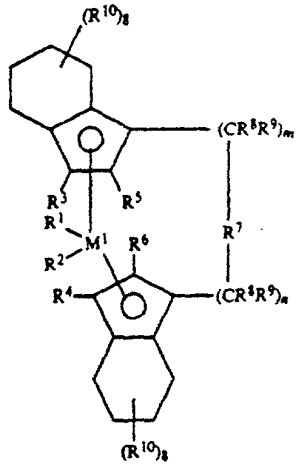
The present invention relates to novel metallocenes which contain ligands of 2-substituted indenyl derivatives and can very advantageously be used as catalysts in the preparation of polyolefins of high melting point (high isotacticity).

Polyolefins of relatively high melting point and thus relatively high crystallinity and relatively high hardness are particularly important as engineering materials (for example large hollow articles, tubes and moldings).

Chiral metallocenes are, in combination with aluminoxanes, active, stereospecific catalysts for the preparation of polyolefins (U.S. Pat. No. 4,769,510). These metallocenes also include substituted indene compounds. Thus, for example, the use of the ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride/aluminoxane catalyst system is known for the preparation of isotactic polypropylene; cf. EP-A 185 918). Both this and numerous other polymerization processes coming under the prior art have, in particular, the disadvantage that, at industrially interesting polymerization temperatures, only polymers of relatively low melting points are obtained. Their crystallinity and thus their hardness are too low for use as engineering materials.

Surprisingly, it has now been found that metallocenes which contain, as ligands, certain 2-substituted indenyl derivatives are suitable catalysts for the preparation of polyolefins of high isotacticity (melting point) and narrow molecular weight distribution.

The present invention therefore provides the compounds of the formula I below



(I)

in which

M^1 is a metal from group IVb, Vb or VIb of the Periodic Table,

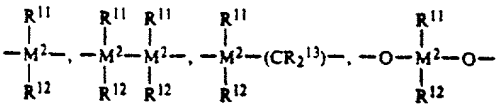
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

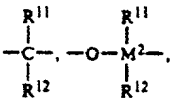
R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, which

may be halogenated, a C_6-C_{10}-aryl group, an $-NR_2^{15}$, $-SR^{15}$, $-OSiR_3^{15}$, $-SiR_3^{15}$ or $-PR_2^{15}$ radical in which R^{15} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and are as defined for R^3 and R^4, with the proviso that R^5 and R^6 are not hydrogen,

R^7 is





$=BR^{11}$, $=AlR^{11}$, $-Ge-$, $-Sn-$, $-O-$, $-S-$, $=SO$, $=SO_2$, $=NR^{11}$, $=CO$, $=PR^{11}$ or $=P(O)R^{11}$,

where

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_6-C_{10}-fluoroaryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^{11} and R^{12} or R^{11} and R^{13}, in each case with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and are as defined for R^{11},

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2, and,

the radicals R^{10} are identical or different and are as defined for R^{11}, R^{12} and R^{13}.

Alkyl is straight-chain or branched alkyl. Halogen (halogenated) is fluorine, chlorine, bromine or iodine, preferably fluorine or chlorine.

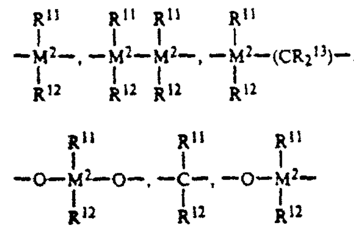
In the formula I, M^1 is a metal from group IVb, Vb or VIb of the Periodic Table, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum or tungsten, preferably zirconium, hafnium or titanium.

R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-, preferably C_1-C_3-alkyl group, a C_1-C_{10}-, preferably C_1-C_3-alkoxy group, a C_6-C_{10}-, preferably C_6-C_8-aryl group, a C_6-C_{10}-, preferably C_6-C_8-aryloxy group, a C_2-C_{10}-, preferably C_2-C_4-alkenyl group, a C_7-C_{40}-, preferably C_7-C_{10}-arylalkyl group, a C_7-C_{40}-, preferably C_7-C_{12}-alkylaryl group, a C_8-C_{40}-, preferably C_8-C_{12}-arylalkenyl group or a halogen atom, preferably chlorine.

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, preferably a fluorine, chlorine or bromine atom, a C_1-C_{10}-, preferably C_1-C_4-alkyl group, which may be halogenated, a C_6-C_{10}-, preferably C_6-C_8-aryl group, an $-NR_2^{15}$, $-SR^{15}$, $-OSiR_3^{15}$, $-SiR_3^{15}$ or $-PR_2^{15}$ radical in which R^{15} is a halogen atom, preferably a chlorine atom, or a C_1-C_{10}-, preferably C_1-C_3-alkyl group or a C_6-C_{10}-, preferably C_6-C_8-aryl group. R^3 and R^4 are particularly preferably hydrogen.

R^5 and R^6 are identical or different, preferably identical, and are as defined for R^3 and R^4, with the proviso that R^5 and R^6 cannot be hydrogen. R^5 and R^6 are preferably (C_1–C_4)-alkyl, which may be halogenated, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl or trifluoromethyl, in particular methyl.

R^7 is



$=BR^{11}$, $=AlR^{11}$, —Ge—, —Sn—, —O—, —S—, $=SO$, $=SO_2$, $=NR^{11}$, $=CO$, $=PR^{11}$ or $=P(O)R^{11}$, where R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1–C_{10}-, preferably C_1–C_4-alkyl group, in particular a methyl group, a C_1–C_{10}-fluoroalkyl group, preferably a CF_3 group, a C_6–C_{10}-, preferably C_6–C_8-aryl group, a C_6–C_{10}-fluoroaryl group, preferably a pentafluorophenyl group, a C_1–C_{10}-, preferably C_1–C_4-alkoxy group, in particular a methoxy group, a C_2–C_{10}-, preferably C_2–C_4-alkenyl group, a C_7–C_{40}-, preferably C_7–C_{10}-arylalkyl group, a C_8–C_{40}-, preferably C_8–C_{12}-arylalkenyl group or a C_7–C_{40}-, preferably C_7–C_{12}-alkylaryl group, or R^{11} and R^{12} or R^{11} and R^{13}, in each case together with the atoms connecting them, form a ring.

M^2 is silicon, germanium or tin, preferably silicon or germanium.

R^7 is preferably $=CR^{11}R^{12}$, $=SiR^{11}R^{12}$, $=GeR^{11}R^{12}$, —O—, —S—, $=SO$, $=PR^{11}$ or $=P(O)R^{11}$.

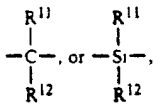
R^8 and R^9 are identical or different and are as define as for R^{11}.

m and n are identical or different and are zero, 1 or 2, preferably zero or 1, where m plus n is zero, 1 or 2, preferably zero or 1.

The radicals R^{10} are identical or different and are as defined for R^{11}, R^{12} and R^{13}. The radicals R^{10} are preferably hydrogen atoms or C_1–C_{10}-, preferably C_1–C_4-alkyl groups.

The particularly preferred metallocenes are thus those in which, in the formula I, M^1 is Zr or Hf, R^1 and

R^2 are identical or different and are methyl or chlorine, R^3 and R^4 are hydrogen, R^5 and R^6 are identical or different and are methyl, ethyl or trifluoromethyl, R^7 is a



radical, n plus m is zero or 1, and R^{10} is hydrogen; in particular the compounds I listed in the working examples.

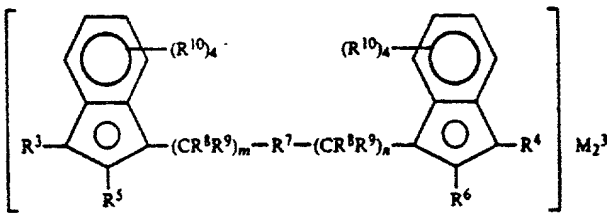
Of the metallocenes I mentioned in the working examples, rac-dimethylsilyl(2-methyl-4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride, rac-ethylene(2-methyl-4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride, racdimethylsilyl(2-methyl-4,5,6,7-tetrahydro-1-indenyl)$_2$dimethylzirconium and rac-ethylene(2-methyl-4,5,6,7-tetrahydro-1-indenyl)$_2$dimethylzirconium are particularly important.

The chiral metallocenes are employed as racemates for the preparation of highly isotactic poly-1-olefins. However, it is also possible to use the pure R- or S-form. These pure stereoisomeric forms allow the preparation of an optically active polymer. However, the meso form of the metallocenes should be separated off since the polymerization-active center (the metal atom) in these compounds is no longer chiral due to mirror symmetry at the central metal, and it is therefore not possible to produce a highly isotactic polymer.

The principle of resolution of the stereoisomers is known.

The present invention furthermore provides a process for the preparation of the metallocenes I, which comprises

a) reacting a compound of the formula II



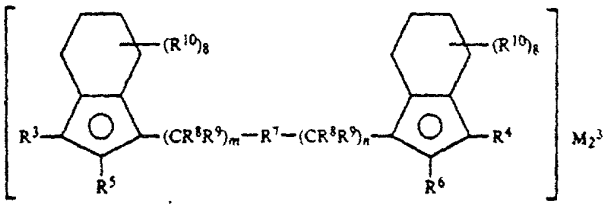
(II)

in which R^3–R^{10}, m and n are defined in the formula I and M^3 is an alkali metal, preferably lithium, with a compound of the formula III

$$M^1X_4 \qquad \text{(III)}$$

in which M^1 is a defined in the formula I, and X is a halogen atom, preferably chlorine, and catalytically hydrogenating the reaction product, or

b) reacting a compound of the formula IIa



(IIa)

with a compound of the formula III

$$M^1X_4 \qquad \text{(III)}$$

in which all the substituents are as defined under a), and, if desired, derivatizing the reaction product obtained under a) or b).

The synthesis is carried out under a protective gas and in anhydrous solvents. The dried salt of the formula II/IIa is added to a suspension of the compound of the formula III in a solvent such as toluene, n-hexane, dichloromethane, ether, THF, n-pentane or benzene, preferably dichloromethane or toluene. The reaction temperature is from −78° C. to 30° C., preferably from −40° C. to 10° C. The reaction duration is from 0.25 to 24 hours, preferably from 1 to 4 hours.

A further embodiment of the process according to the invention comprises replacing the compound III, M^1X_4, by a compound of the formula IIIa, $M^1X_4L_2$. In this formula, L is a donor ligand. Examples of suitable donor ligands are tetrahydrofuran, diethyl ether, dimethyl ether, inter alia, preferably tetrahydrofuran (THF).

In this case, a solution of the salt of the formula II/IIa in one of the abovementioned solvents is added to a solution or suspension of a compound of the formula IIIa in a solvent such as toluene, xylene, ether or THF, preferably THF. However, an alternative procedure is to simultaneously add both components dropwise to a solvent. This is the preferred procedure. The reaction temperature is from −40° C. to 100° C., preferably from 0° C. to 50° C., in particular from 10° C. to 35° C. The reaction duration is from 0.25 hour to 48 hours, preferably from 1 hour to 24 hours, in particular from 2 hours to 9 hours.

The hydrogenation is carried out in a dry, anhydrous solvent such as H_2CCl_2 or glyme. The reaction temper-

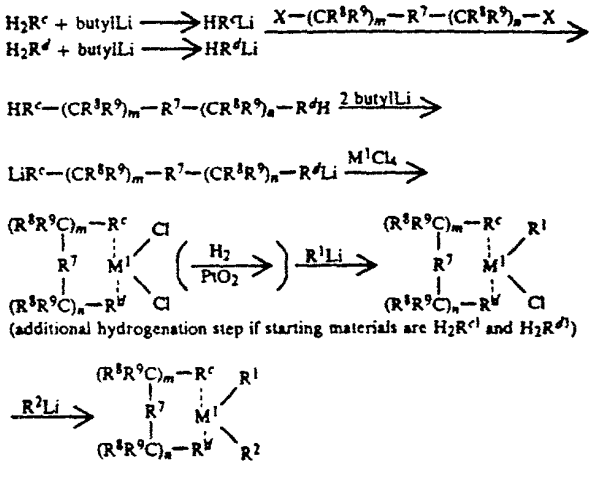
ature is 20° to 70° C., preferably from ambient temperature to 50° C., the pressure is from 5 to 200 bar, preferably from 20 to 120 bar, in particular from 35 to 100 bar, and the reaction duration is from 0.25 to 24 hours, preferably from 0.5 to 18 hours, in particular from 1 to 12 hours. Hydrogenation reactors which can be used are steel autoclaves. The hydrogenation catalyst used is platinum, platinum oxide, palladium or another conventional transition-metal catalyst.

The halogen derivatives obtained in this way can be converted into the alkyl, aryl or alkenyl complexes by known standard methods.

The compounds of the formulae II and IIa are synthesized by deprotonation. This reaction is known; cf. J. Am. Chem. Soc., 112 (1990) 2030–2031, ibid. 110 (1988) 6255–6256, ibid. 109 (1987), 6544–6545, J. Organomet. Chem., 322 (1987) 65–70, New. J. Chem. 14 (1990) 499–503 and the working examples.

The synthesis of the protonated forms of the compounds of these formulae has also been described, with the difference that they are not correspondingly substituted in the α- and β-positions (Bull. Soc. Chim., 1967, 2954). The bridging units required for their synthesis are generally commercially available, but the indenyl compounds required, by contrast, are not. Some literature references containing synthesis procedures are indicated; the procedure for indene derivatives which are not mentioned is analogous: J. Org. Chem., 49 (1984) 4226–4237, J. Chem. Soc., Perkin II, 1981, 403–408, J. Am. Chem. Soc., 106 (1984) 6702, J. Am. Chem. Soc., 65 (1943) 567, J. Med. Chem., 30 (1987) 1303–1308, Chem. Ber. 85 (1952) 78–85 and the working examples.

The metallocenes I can thus in principle be prepared in accordance with the reaction scheme below:



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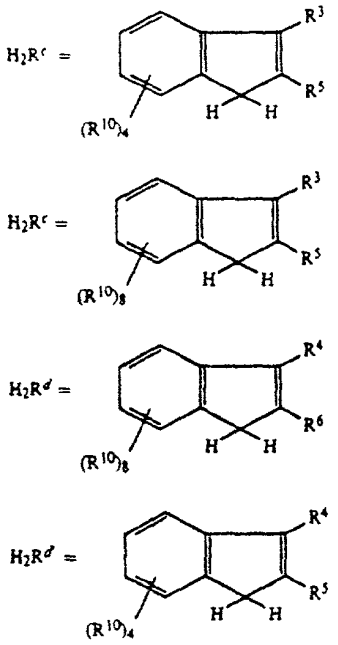
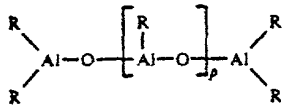
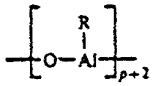


The cocatalyst used according to the invention in the polymerization of olefins is an aluminoxane of the formula (IV)



(IV)

for the linear type and/or of the formula (V)



for the cyclic type, where, in the formulae (IV) and (V), the radicals R may be identical or different and are a C_1-C_6-alkyl group, a C_6-C_{18}-aryl group or hydrogen, and p is an integer from 2 to 50, preferably from 10 to 35.

The radicals R are preferably identical and are methyl, isobutyl, phenyl or benzyl, particularly preferably methyl.

If the radicals R are different, they are preferably methyl and hydrogen or alternatively methyl and isobutyl, preferably from 0.01 to 40% (of the number of radicals R) being hydrogen or isobutyl.

The aluminoxane can be prepared in different ways by known processes. One of the methods is, for example, the reaction of an aluminum-hydrocarbon compound and/or a hydridoaluminum-hydrocarbon compound with water (gaseous, solid, liquid or bound—for example as water of crystallization) in an inert solvent (such as, for example, toluene). In order to prepare an aluminoxane containing different alkyl groups R, two different trialkylaluminum compounds ($AlR_3 + AlR'_3$) in accordance with the desired composition are reacted

with water (cf. S. Pasynkiewicz, Polyhedron 9 (1990) 429 and EP-A 302 424).

The precise structure of the aluminoxanes IV and V is not known.

Irrespective of the preparation method, a varying content of unreacted aluminum starting compound, in free form or as an adduct, is common to all the aluminoxane solutions.

It is possible to preactivate the metallocene I using an aluminoxane of the formula (IV) and/or (V) before use in the polymerization reaction. This considerably increases the polymerization activity and improves the particle morphology.

The preactivation of the transition-metal compound is carried out in solution. The metallocene is preferably dissolved in a solution of the aluminoxane in an inert hydrocarbon. Suitable inert hydrocarbons are aliphatic or aromatic hydrocarbons. Toluene is preferred.

The concentration of the aluminoxane in the solution is in the range from about 1% by weight up to the saturation limit, preferably from 5 to 30% by weight, in each case based on the entire solution. The metallocene can be employed in the same concentration, but is preferably employed in an amount of from 10^{-4}—1 mol per mole of aluminoxane. The preactivation time is from 5 minutes to 60 hours, preferably from 5 to 60 minutes. The preactivation temperature is from −78° C. to 100° C., preferably from 0 to 70° C.

The metallocene can also be prepolymerized or applied to a support. The prepolymerization is preferably carried out using the olefin (or one of the olefins) employed in the polymerization.

Examples of suitable supports are silica gels, aluminum oxides, solid aluminoxane or other inorganic support materials. Another suitable support material is a polyolefin powder in finely divided form.

A further possible variation of the process comprises using a salt-like compound of the formula $R_xNH_{4-x}BR'_4$ or of the formula $R_3PHBR'_4$ as cocatalyst instead of or in addition to an aluminoxane. x here

is 1, 2 or 3, the R radicals are identical or different and are alkyl or aryl, and R' is aryl, which may also be fluorinated or partially fluorinated. In this case, the catalyst comprises the product of the reaction of a metallocene with one of said compounds (cf. EP-A 277 004).

The polymerization or copolymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or batchwise, in one or more steps, at a temperature of from 0° to 150° C., preferably from 30° to 80° C. Olefins of the formula R^a—CH=CH—R^b are polymerized or copolymerized. In this formula, R^a and R^b are identical or different and are a hydrogen atom or an alkyl radical having 1 to 14 carbon atoms.

However, R^a and R^b, together with the carbon atoms connecting them, may also form a ring. Examples of such olefins are ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, norbornene or norbornadiene. In particular, propylene and ethylene are polymerized.

The molecular weight regulator added, if necessary, is hydrogen. The overall pressure in the polymerization system is from 0.5 to 100 bar. The polymerization is preferably carried out in the industrially particularly interesting pressure range of from 5 to 64 bar.

The metallocene is used in a concentration, based on the transition metal, of from 10^{-3} to 10^{-8}, preferably from 10^{-4} to 10^{-7} mol of transition metal per dm^3 of solvent or per dm^3 of reactor volume. The aluminoxane is used in a concentration of from 10^{-5} to 10^{-1} mol, preferably from 10^{-4} to 10^{-2} mol, per dm^3 of solvent or per dm^3 of reactor volume. In principle, however, higher concentrations are also possible.

If the polymerization is carried out as a suspension or solution polymerization, an inert solvent which is customary for the Ziegler low-pressure process is used. For example, the polymerization is carried out in an aliphatic or cycloaliphatic hydrocarbon; examples of these which may be mentioned are butane, pentane, hexane, heptane, isooctane, cyclohexane and methylcyclohexane.

It is also possible to use a petroleum ether or hydrogenated diesel oil fraction. Toluene can also be used.

The polymerization is preferably carried out in the liquid monomer.

If inert solvents are used, the monomers are metered in in gaseous or liquid form.

The polymerization can have any desired duration since the catalyst system to be used according to the invention exhibits only a low time-dependent drop in polymerization activity.

The process is distinguished by the fact that the metallocenes according to the invention give, in the industrially interesting temperature range of between 30° and 80° C, polymers of high molecular weight, high stereospecificity, narrow molecular weight dispersity and, in particular, high melting point, which is to say high crystallinity and high hardness.

The examples below are intended to illustrate the invention in greater detail.

The following abbreviations are used:

VN =	viscosity number in cm^3/g	
M_w =	weight average molecular weight	determined by gel permeation chromatography
M_w/M_n =	molecular weight dispersity	

-continued

II =	isotactic index (II = mm + ½ mr), determined by ^{13}C-NMR spectroscopy
n_{iso} =	length of the isotactic blocks (in propylene units) (n_{iso} = 1 + 2 mm/mr), determined by ^{13}C-NMR spectroscopy

The melting points and heats of melting ΔH_{melt} were determined using DSC (heating and cooling rate 20° C./min).

Synthesis of the starting substances

I) Synthesis of 2-Me-indene

110.45 g (0.836 mol) of 2-indanone were dissolved in 500 ml of diethyl ether, and 290 cm^3 of 3N (0.87 mol) ethereal methylGrignard solution were added dropwise at such a rate that the mixture refluxed gently. After the mixture had boiled for 2 hours under gentle reflux, it was transferred onto an ice/hydrochloric acid mixture, and a pH of 2-3 was established using ammonium chloride. The organic phase was separated off, washed with $NaHCO_3$ and sodium chloride solution and dried, giving 98 g of crude product (2-hydroxy-2-methylindane), which was not purified further.

This product was dissolved in 500 cm^3 of toluene, 3 g of p-toluenesulfonic acid were added, and the mixture was heated on a water separator until the elimination of water was complete, and was evaporated, the residue was taken up in dichloromethane, the dichloromethane solution was filtered through silica gel, and the filtrate was distilled in vacuo (80° C./10 mbar).

Yield: 28.49 g (0.22 mol/26%).

The synthesis of this compound is also described in: C. F. Koelsch, P. R. Johnson, J. Am. Chem. Soc., 65 (1943) 567-573.

II) Synthesis of $(2\text{-Me-indene})_2SiMe_2$

13 g (100 mmol) of 2-Me-indene were dissolved in 400 cm^3 of diethyl ether, and 62.5 cm^3 of 1.6N (100 mmol) n-butyllithium/n-hexane solution were added dropwise over the course of 1 hour with ice cooling, and the mixture was then stirred at ~35° C. for a further 1 hour.

6.1 cm^3 (50 mmol) of dimethyldichlorosilane were introduced into 50 cm^3 of Et_2O, and the lithio salt solution was added dropwise at 0° C. over the course of 5 hours, the mixture was stirred overnight at room temperature and left to stand over the weekend.

The solid which had deposited was filtered off, and the filtrate was evaporated to dryness. The product was extracted using small portions of n-hexane, and the extracts were filtered and evaporated, giving 5.7 g (18.00 mmol) of white crystals. The mother liquor was evaporated, and the residue was then purified by column chromatography (n-hexane/H_2CCl_2 9:1 by volume), giving a further 2.5 g (7.9 mmol/52%) of product (as an isomer mixture).

R_f (SiO_2; n-hexane/H_2CCl_2 9:1 by volume)=0.37.

The ^{1}H-NMR spectrum exhibits the signals expected for an isomer mixture with respect to shift and integration ratio.

III) Synthesis of $(2\text{-Me-Ind})_2CH_2CH_2$

3 g (23 mmol) of 2-Me-indene were dissolved in 50 cm^3 of THF, 14.4 cm^3 of 1.6N (23.04 mmol) n-butyllithium/n-hexane solution were added dropwise, and the mixture was then stirred at 65° C. for 1 hour. 1 cm^3 (11.5 mmol) of 1,2-dibromoethane was then added at −78° C., and the mixture was allowed to warm to room temperature and was stirred for 5 hours. The mixture was evaporated, and the residue was purified by column

chromatography (SiO_2; n-hexane/H_2CCl_2 9:1 by volume).

The fractions containing the product were combined and evaporated, the residue was taken up in dry ether, the solution was dried over $MgSO_4$ and filtered, and the solvent was stripped off.

Yield: 1.6 g (5.59 mmol/49%) of isomer mixture R_f (SiO_2; n-hexane/H_2CCl_2 9:1 by volume)=0.46.

The ^{1}H-NMR spectrum corresponds to expectations for an isomer mixture in signal shift and integration.

Synthesis of the metallocenes I

IV) rac-Dimethylsilyl(2-Me-4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride

a. Synthesis of the precursor rac-dimethylsilyl(2-Me-1-idenyl)$_2$zirconium dichloride

1.68 g (5.31 mmol) of the chelate ligand dimethylsilyl(2-methylindene)$_2$ were introduced into 50 cm^3 of THF, and 6.63 cm^3 of a 1.6N (10.61 mmol) n-BuLi/n-hexane solution were added dropwise at ambient temperature over the course of 0.5 hour. The mixture was stirred for 2 hours at about 35° C., the solvent was stripped off in vacuo, and the residue was stirred with n-pentane, filtered off and dried.

The dilithio salt obtained in this way was added at −78° C. to a suspension of 1.24 g (5.32 mmol) of ZrCl in 50 cm^3 of CH_2Cl_2, and the mixture was stirred at this temperature for 3 hours. The mixture was then warmed to room temperature overnight and evaporated. The ^{1}H-NMR spectrum showed, in addition to the presence of some $ZrCl_4(thf)_2$, a rac/meso mixture. After stirring with n-pentane and drying, the solid, yellow residue was suspended in THF, filtered off and examined by NMR spectroscopy. These three working steps were repeated a number of times; finally, 0.35 g (0.73 mmol/14%) of product was obtained in which the rac form, according to ^{1} H-NMR, was enriched to more than 17:1.

The compound exhibited a correct elemental analysis and the following NMR signals ($CDCl_3$, 100 MHz): δ=1.25 (s, 6H, Si-Me); 2.18 (s, 6H, 2-Me); 6.8 (s, 2H, 3-H-Ind); 6.92–7.75 (m, 8H, 4-7-H-Ind).

b. Synthesis of the end product

0.56 g (1.17 mmol) of the precursor rac-dimethylsilyl(2-Me-1-indenyl)$_2$zirconium dichloride were dissolved in 70 cm^3 of CH_2Cl_2 and the solution was introduced, together with 40 mg of PtO_2, into a 200 cm^3 NOVA stirred autoclave. The mixture was then stirred at room temperature for 4 hours under an H_2 pressure of 40 bar. The filtrate was evaporated, the residue was washed with toluene/n-hexane (1:2 by volume), filtered and evaporated. N-pentane was added, and the suspension obtained was filtered off and dried. The yield was 0.34 g (0.7 mmol/60%). The ^{1}H-NMR spectrum (CD_2Cl_2, 100 MHz) showed the following signals:

δ=0.90 (s, 6H, Me-Si); 1.43–1.93 (m, 8H, indenyl-H); 2.10 (s, 6H, 2-Me); 2.44–3.37 (m, 8H, indenyl-H); 6.05 (s, 2H, 3-H-Ind).

V) Synthesis of rac-ethylene(2-Me-4,5,6,7-tetrahydro1-indenyl)$_2$zirconium dichloride

a. Synthesis of the precursor rac-ethylene(2-Me-1-indenyl)$_2$zirconium dichloride

14.2 cm^3 of 2.5N (35.4 mmol) n-BuLi/n-hexane solution were added dropwise over the course of 1 hour at room temperature to 5.07 g (17.7 mmol) of the ligand ethylene(2-methylindene)$_2$ in 200 cm^3 of THF, and the mixture was then stirred at about 50° C. for 3 hours. A precipitate which formed temporarily dissolved again. The mixture was left to stand overnight.

6.68 g (17.7 mmol) of $ZrCl_4(thf)_2$ in 250 cm^3 of THF were added dropwise, simultaneously with the above dilithio salt solution, to about 50 cm^3 of THF at 50° C., and the mixture was then stirred at this temperature for 20 hours. The toluene extract of the evaporation residue was evaporated. The residue was extracted with a little THF, and the product was recrystallized from toluene, giving 0.44 g (0.99 mmol/5.6%) of product in which the rac form was enriched to more than 15:1.

The compound exhibited a correct elemental analysis and the following NMR signals ($CDCl_3$, 100 MHz): $\delta = 2.08$ (2s, 6H, 2-Me); 3.45–4.18 (m, 4H, $—CH_2CH_2—$); 6.65 (2H, 3-H-Ind); 7.05–7.85 (m, 8H, 4-7-H-Ind).

b. Synthesis of the end product

56 g (1.25 mmol) of rac-ethylene(2-Me-1-indenyl)$_2$-zirconium dichloride was dissolved in 50 cm^3 of CH_2Cl_2, and the solution was introduced, together with 40 mg of PtO_2, into a 200 cm^3 NOVA stirred autoclave. The mixture was then stirred at room temperature for 2 hours under an H_2 pressure of 40 bar and evaporated to dryness, and the residue was sublimed in a high vacuum at a bath temperature of about 100° C., giving 0.46 g (1.01 mmol/81%) of product. The elemental analysis was correct, and the ^{1}H-NMR spectrum showed the following signals: $\delta = 1.46$–1.92 (m, 8H, indenyl-H), 2.14 (s, 6H, 2-Me); 2.49–2.73 (m, 6H, indenyl-H and $—CH_2CH_2—$), 2.89–3.49 (m, 6H, indenyl-H); 6.06 (s, 2H, 3-H-Ind).

VI) $Me_2Zr[(2\text{-}Me\text{-}4,5,6,7\text{-}H_4\text{-}Ind)_2CH_2CH_2]$

5 cm^3 of 1.6N (8 mmol) of ethereal methyllithium solution were added dropwise at −50° C. to 1.27 g (2.79 mmol) of $Cl_2Zr[(2\text{-}Me\text{-}4,5,6,7\text{-}H_4\text{-}Ind)_2CH_2CH_2]$ in 20 cm^3 of Et_2O, and the mixture was then stirred for 1 hour at −10° C. The solvent was replaced by n-hexane, and the mixture was stirred for a further 2 hours at room temperature, filtered and evaporated.

Yield: 1 g (2.40 mmol/86%); correct elemental analysis.

VII) $Me_2Zr[(2\text{-}Me\text{-}4,5,6,7\text{-}H_4\text{-}Ind)_2SiMe_2]$

4.3 cm^3 of 1.6N (6.88 mmol) of ethereal methyllithium solution were added dropwise over the course of 15 minutes at −35° C. to 1.33 g (2.74 mmol) of $Cl_2Zr[(2\text{-}Me\text{-}4,5,6,7\text{-}H_4\text{-}Ind)_2SiMe_2]$ in 25 cm^3 of Et_2O. The mixture was stirred for 1 hour, the solvent was replaced by n-hexane, the mixture was stirred for 2 hours at 10° C. and then filtered, the filtrate was evaporated, and the residue was sublimed in a high vacuum.

Yield: 1.02 g (2.49 mmol/89%); correct elemental analysis

VIII) $Cl_2Zr[(2\text{-}Me\text{-}4,5,6,7\text{-}H_4\text{-}Ind)_2SiMePh]$

1.5 g (2.78 mmol) of $Cl_2Zr[(2\text{-}Me\text{-}Ind)_2SiMePh]$ and 60 mg of PtO_2 in 80 cm^3 of H_2CCl_2 were hydrogenated for 5 hours at 40° C. in a stirred autoclave under an H_2 pressure of 30 bar. The mixture was filtered, the solvent was stripped off, and the residue was sublimed in a high vacuum.

Yield: 0.71 g (1.30 mmol/47%); correct elemental analysis

IX) $Cl_2Zr[(2\text{-}Me\text{-}4,5,6,7\text{-}H_4\text{-}Ind)_2SiPh_2]$

0.8 g (1.33 mmol) of $Cl_2Zr[(2\text{-}Me\text{-}Ind)_2SiPh_2]$, dissolved in 50 cm^3 of H_2CCl_2, were stirred for 3 hours at 40° C. with 30 mg of Pt under an H_2 pressure of 50 bar. The mixture was filtered, the filtrate was evaporated, the residue was washed with warm n-hexane, the mixture was filtered, and the filtrate was evaporated.

Yield: 0.36 g (0.59 mmol/44%); correct elemental analysis

X) $Cl_2Zr[(2\text{-}Et\text{-}4,5,6,7\text{-}H_4\text{-}Ind)_2CH_2CH_2]$

1.09 g (2.30 mmol) of $Cl_2Zr[(2\text{-Et-Ind})_2CH_2CH_2]$ in 80 cm^3 of H_2CCl_2 were hydrogenated for 1 hour at ambient temperature together with 50 mg of PtO_2 under an H_2 pressure of 80 bar. The mixture was filtered, the filtrate was evaporated, and the residue was sublimed in a high vacuum.

Yield: 0.94 g (1.95 mmol/85%); correct elemental analysis

XI) $Cl_2Zr[(2\text{-Et-4,5,6,7-H}_4\text{-Ind})_2SiMe_2]$

2.00 g (3.96 mmol) of $Cl_2Zr[(2\text{-Et-Ind})_2SiMe_2]$in 100 cm^3 of H_2CCl_2 were hydrogenated for 3 hours at 35° C. together with 60 mg of PtO_2 under an H_2 pressure of 50 bar. The mixture was filtered, the filtrate was evaporated, and the residue was recrystallized from n-pentane.

Yield: 1.41 g (2.75 mmol/69%); correct elemental analysis

XII) $Cl_2Zr[(2\text{-Me-4,5,6,7-H}_4\text{-Ind})_2CHMeCH_2]$

0.80 g (1.73 mmol) of $Cl_2Zr[(2\text{-Me-Ind})_2CHMeCH_2]$ in 40 cm^3 of H_2CCl_2 were stirred for 1 hour at ambient temperature together with 30 mg of PtO_2 under an H_2 pressure of 80 bar, the mixture was then filtered, the filtrate was evaporated, and the residue was sublimed.

Yield: 0.55 g (1.17 mmol/68%); correct elemental analysis

XIII) $Cl_2Zr[(2\text{-Me-4,5,6,7-H}_4\text{-Ind})_2CMe_2]$

0.3 g (0.65 mmol) of $Cl_2Zr[(2\text{-Me-Ind})_2CMe_2]$ in 30 cm^3 of H_2CCl_2 were hydrogenated for 1 hour at ambient temperature together with 30 mg of Pt under an H_2 pressure of 70 bar. The solvent was stripped off, and the residue was sublimed in a high vacuum.

Yield: 0.21 g (0.45 mmol/69%); correct elemental analysis

Abbreviations:

Me = methyl, Et = ethyl, Bu = butyl, Ph = phenyl,

Ind = indenyl, THF = tetrahydrofuran, PP = polypropylene,

PE = polyethylene.

Metallocenes I as catalysts for the polymerization of olefins

Example 1

12 dm^3 of liquid propylene were introduced into a dry 24 dm^3 reactor which had been flushed with nitrogen. 35 cm^3 of a toluene solution of methylaluminoxane (corresponding to 52 mmol of Al, mean degree of oligomerization n = 17) were then added, and the batch was stirred at 30° C. for 15 minutes. In parallel, 5.3 mg (0.011 mmol) of rac-dimethylsilyl(2-Me-4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride were dissolved in 13.5 cm^3 of a toluene solution of methylaluminoxane (20 mmol of Al) and preactivated by standing for 15 minutes. The solution was then introduced into the reactor and the polymerization system was heated to 70° C. (over the course of 5 minutes) and kept at this temperature for 3 hours by cooling.

The activity of the metallocene was 50.3 kg of PP/g of metallocene × h.

VN = 37 cm^3/g; M_w = 24 300 g/mol; M_w/M_n = 2.4; II = 96.0%; n_{iso} = 62; M.p. = 150° C.; ΔH_{melt} = 104 J/g.

Example 2

Example 1 was repeated, but 19.5 mg (0.04 mmol) of the metallocene were employed, and the polymerizaton temperature was 50° C.

The activity of the metallocene was 18.8 kg of PP/g of metallocene × h.

VN=72 cm^3/g; M_w=64 750 g/mol; M_w/M_n=2.1; II=96.0%; n_{iso}=64; M.p.=154° C.; ΔH_{melt}=109.5 J/g.

Example 3

Example 1 was repeated, but 58.0 mg (0.12 mmol) of the metallocene were used and the polymerization temperature was 30° C.

The activity of the metallocene was 9.7 kg of PP/g of metallocene×h.

VN=152 cm^3/g; M_w=171 000 g/mol; M_2/M_n=2.2; II=99.9%; n_{iso}=>500; M.p.=160° C.; ΔH_{melt}=103 J/g.

Comparative Examples A-H

Examples 1 to 3 were repeated, but the metallocenes dimethylsilyl(2-Me-1-indenyl)$_2$zirconium dichloride (metallocene 1), dimethylsilyl(4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride (metallocene 2) and dimethylsilyl(1-indenyl)$_2$zirconium dichloride (metallocene 3) were used.

Comp. Ex.	Metallocene	Polym. temp. [°C.]	n_{iso}	M.p. [°C.]	ΔH_{melt} [J/g]
A	1	70	38	145	86.6
B	1	50	48	148	88.1
C	1	30	48	152	90.2
D	2	70	34	141	—
E	2	50	38	143	—
F	3	70	32	140	—
G	3	50	34	142	—
H	3	30	37	145	—

Comparison of Comparative Examples F/G with D/E confirms the positive effect of the 4,5,6,7-tetrahydroindenyl ligand compared with indenyl, and Comparative Examples F/G/H compared with A/B/C show the positive effect of the substitution in the 2-position of the indenyl ligand.

In comparison with Examples 1 to 3, however, only the combination of substitution in the 2-position together with the tetrahydroindenyl system results in very high melting points and heats of melting and thus in high crystallinity and hardness of the polymers.

Example 4

Example 1 was repeated, but 6.8 mg (0.015 mmol) of ethylene(2-Me-4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride were employed.

The metallocene activity was 72.5 kg of PP/g of metallocene×h.

VN=35 cm^3/g; M_w=20 750 g/mol; M_w/M_n=1.9; II=94.5%; n_{iso}=34; M.p.=141° C.; ΔH_{melt}=92.4 J/g.

Example 5

Example 4 was repeated, but 28.1 mg (0.062 mmol) of the metallocene were used and the polymerization temperature was 50° C.

The metallocene activity was 28.5 kg of PP/g of metallocene×h.

VN=51 cm^3/g; M_w=28 200 g/mol; M_w/M_n=2.2; II=94.8%; n_{iso}=35; M.p.=143° C.; ΔH_{melt}=97.9 J/g.

Example 6

Example 4 was repeated, but 50 mg (0.110 mmol) of the metallocene were used and the polymerization temperature was 30° C.

The metallocene activity was 10.9 kg of PP/g of metallocene×h.

VN=92 cm^3/g; M_w=93 800 g/mol; M_w/M_n=2.2; II=95.5%; n_{iso}=48; M.p.=151° C.; ΔH_{melt}=99.0 J/g.

Comparative Examples I–O

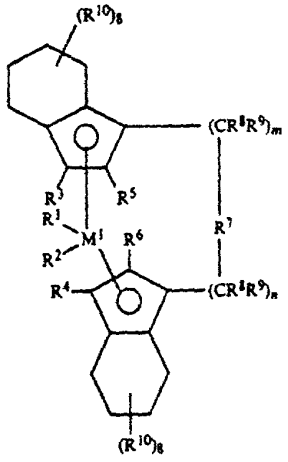
Examples 4 to 6 were repeated, but the metallocenes ethylene(1-indenyl)$_2$zirconium dichloride (metallocene 4) and ethylene(2-Me-1-indenyl)$_2$zirconium dichloride (metallocene 5) were used.

Comp. Ex.	Metallocene	Polym. temp. [°C.]	n_{iso}	M.p. [°C.]	ΔH_{melt} [J/g]
I	4	70	23	132	64.9
K	4	50	30	138	78.1
L	4	30	29	137	78.6
M	5	70	25	134	77.0
N	5	50	30	138	78.9
O	5	30	32	138	78.6

Comparison of Comparative Examples I to O with Examples 4 to 6 confirms the effect of the substitution in the 2-position together with the use of the tetrahydroindenyl system. n_{iso}, melting point and heat of melting are significantly higher in each of Examples 4–6, and the crystallinity and hardness of the polymers are thus also significantly improved.

We claim:

1. A compound of the formula I for preparing essentially isotactic olefin polymers



in which

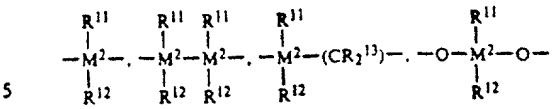
M^1 is a metal from group IVb, Vb or VIb of the Periodic Table

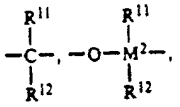
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1–C_{10}-alkyl group, a C_1–C_{10}-alkoxy group, a C_6–C_{10}-aryl group, a C_6–C_{10}-aryloxy group, a C_2–C_{10}-alkenyl group, a C_7–C_{40}-arylalkyl group, a C_7–C_{40}-alkylaryl group, a C_8–C_{40}-arylalkenyl group or a halogen atom,

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a halogen atom, a C_1–C_{10}-alkyl group, which is optionally halogenated, a C_6–C_{10}-aryl group, an $—NR_2^{15}$, $—SR^{15}$, $—OSiR_3^{15}$, $—SiR_3^{15}$ or $—PR_2^{15}$ radical in which R^{15} is a halogen atom, a C_1–C_{10}-alkyl group or a C_6–C_{10}-aryl group,

R^5 and R^6 are identical or different and are as defined for R^3 and R^4, with the proviso that R^5 and R^6 are not hydrogen,

R^7 is





$$=BR^{11},\ =AlR^{11},\ -Ge-,\ -Sn-,\ -O-,\ -S-,\ =SO,$$

$$=SO_2,\ =NR^{11},\ =CO,\ =PR^{11}\ \text{or}\ =P(O)R^{11},$$

where

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1–C_{10}-alkyl group, a C_1–C_{10}-fluoroalkyl group, a C_6–C_{10}-aryl group, a C_6–C_{10}-fluoroaryl group, a C_1–C_{10}-alkoxy group, a C_2–C_{10}-alkenyl group, a C_7–C_{40}-arylalkyl group, a C_8–C_{40}-arylalkenyl group or a C_7–C_{40}-alkylaryl group, or R^{11} and R^{12} or R^{11} and R^{13}, in each case with the atoms connecting them, form a ring,

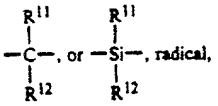
M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and are as defined for R^{11}

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2, and

the radicals R^{10} are identical or different and are as defined for R^{11}, R^{12} and R^{13}.

2. A compound of the formula I as claimed in claim 1, wherein, in the formula I, M^1 is Zr or Hf, R^1 and R^2 are identical or different and are methyl or chlorine, R^3 or R^4 are hydrogen, R^5 and R^6 are identical or different and are methyl, ethyl or trifluoromethyl, R^7 is a



n plus m is zero or 1, and R^{10} is hydrogen.

3. A compound of the formula I as claimed in claim 1 wherein the compound is rac-dimethylsilyl(2-methyl-4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride, rac-ethylene(2-methyl-4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride, rac-dimethylsilyl (2-methyl-4,5,6,7-tetrahydro-1-indenyl)$_2$dimethylzirconium or rac-ethylene(2-methyl-4,5,6,7-tetrahydro-1-indenyl)$_2$dimethylzirconium.

4. A compound as claimed in claim 1, wherein M^1 is zirconium, hafnium or titanium.

5. A compound as claimed in claim 1, wherein R^1 and R^2 are identical or different and are a hydrogen atom, a C_1–C_3-alkyl group, a C_1–C_3-alkoxy group, a C_6–C_8-aryl group, a C_6–C_8-aryloxy group, a C_2–C_4-alkenyl group, a C_7–C_{10}-arylalkyl group, a C_7–C_{12}-alkylaryl group, a C_8–C_{12}-arylalkenyl group or chlorine.

6. A compound as claimed in claim 1, wherein R^3 and R^4 are identical or different and are a hydrogen atom, a fluorine, chlorine or bromine atom, a C_1–C_4-alkyl group which may be halogenated, a C_6–C_8-aryl group, a $-NR_2^{15}$, $-SR^{15}$, $-OSiR_3^{15}$, $-SiR_3^{15}$ or $-PR_2^{15}$ radical in which R^{15} is a chlorine atom, or a C_1–C_3-alkyl group or a C_6–C_8-aryl group.

7. A compound as claimed in claim 1, wherein R^3 and R^4 are hydrogen.

8. A compound as claimed in claim 1, wherein R^5 and R^6 are identical.

9. A compound as claimed in claim 1, wherein R^5 and R^6 are (C_1-C_4)-alkyl, which may be halogenated with methyl.

10. A compound as claimed in claim 1, wherein R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_4-alkyl group, a CF_3 group, a C_6-C_8-aryl group, a pentafluorophenyl group, a C_1-C_4-alkoxy group, a C_2-C_4-alkenyl group, a C_7-C_{10}-arylalkyl group, a C_8-C_{12}-arylalkenyl group or a C_7-C_{12}-alkylaryl group, or R^{11} and R^{12} or R^{11} and

R^{13}, in each case together with the atoms connecting them, form a ring.

11. A compound as claimed in claim **1**, wherein M^2 is silicon or germanium.

12. A compound as claimed in claim **1**, wherein R^7 is $=CR^{11}R^{12}$, $=SiR^{11}R^{12}$, $=GeR^{11}R^{12}$, —O—, —S—, =SO, $=PR^{11}$ or $=P(O)R^{11}$.

13. A compound as claimed in claim **1**, wherein m and n are identical or different and are zero or 1.

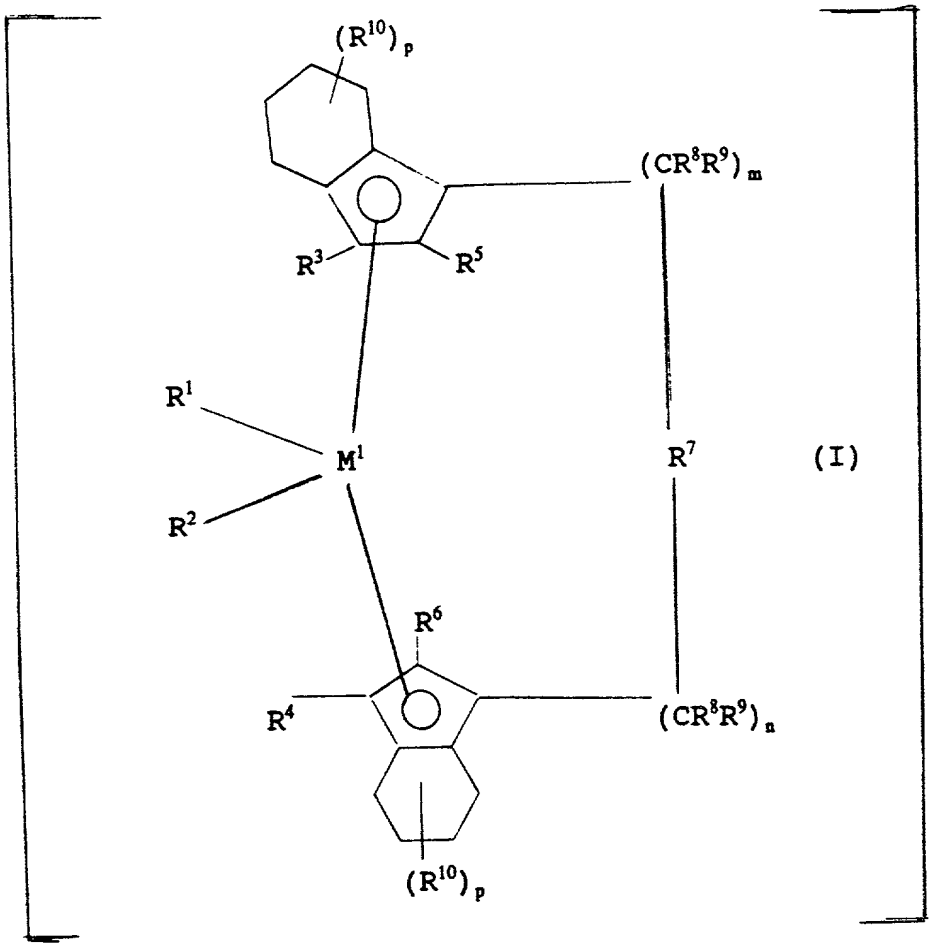
14. A compound as claimed in claim **1**, wherein m plus n is zero or 1.

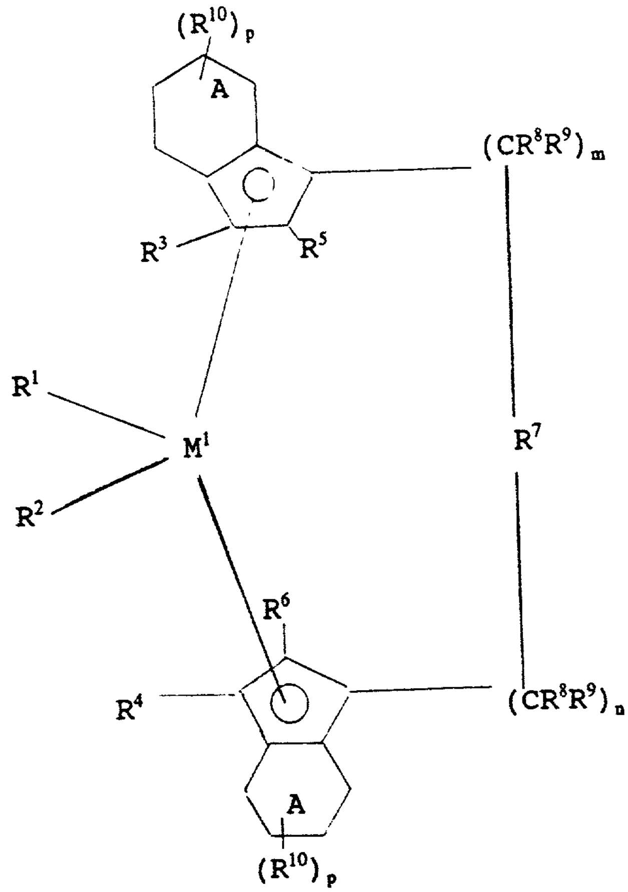
15. A compound as claimed in claim **1**, wherein R^{10} is hydrogen or C_1-C_4-alkyl groups.

* * * * *

We claim:

1. A compound of the formula I [for preparing essentially isotactic olefin polymers]





(I)

in which

M^1 is a metal from group IVb, Vb or VIb of the Periodic Table

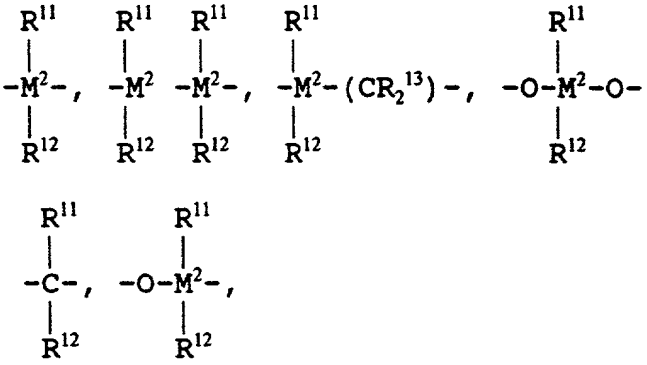
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a halogen atom, a C_1-C_{10}-alkyl group, which is optionally halogenated, a C_6-C_{10}-aryl group, an $-NR_2^{15}$, $-SR^{15}$, $-OSiR_3^{15}$, $-SiR_3^{15}$ or $-PR_2^{15}$

radical in which R^{15} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and are as defined for R^3 and R^4, with the proviso that R^5 and R^6 are not hydrogen,

R^7 is



$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $=P(O)R^{11}$,

where

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_6-C_{10}-fluoroaryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or a pair of substituents R^{11} and R^{12} or R^{11} and R^{13} in each case with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and are as defined for R^{11}

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2, [and]

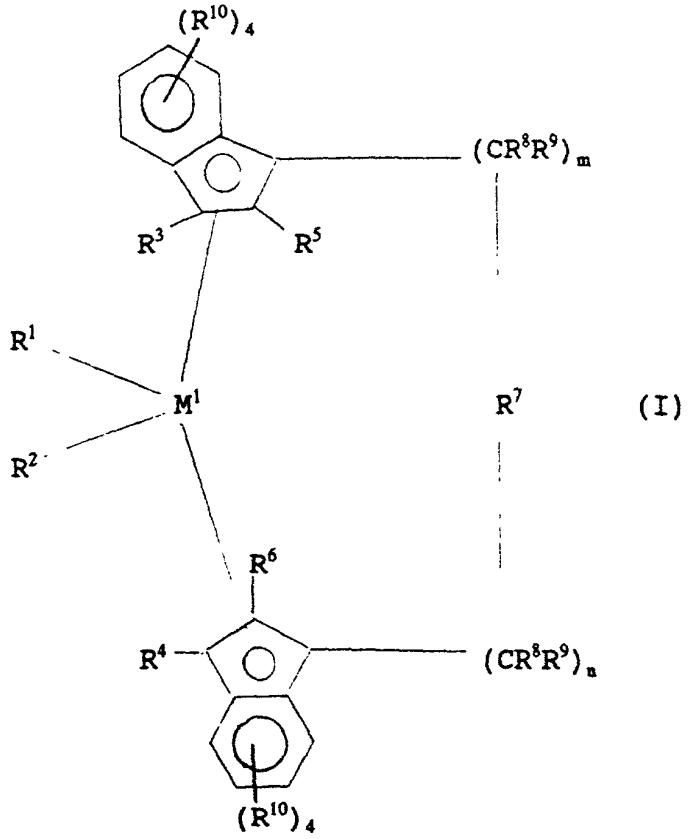
the radicals R^{10} are identical or different and are as defined for R^{11}, R^{12} and R^{13},

rings A are saturated or aromatic,

p is 8, when rings A are saturated, and

p is 4, when rings A are aromatic.

16. A compound of the formula I



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in which

M^1 is a metal from group IVb, Vb or VIb of the Periodic Table,

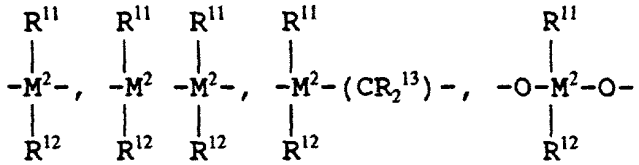
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

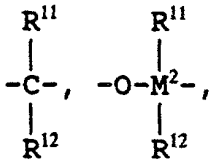
R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, which is optionally halogenated, a C_6-C_{10}-aryl group, an $-NR_2^{15}$, $-SR^{15}$, $-OSiR_3^{15}$, $-SiR_3^{15}$ or PR_2^{15} radical in which R^{15} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and are as defined for R^3

and R^4, with the proviso that R^5 and R^6 are not both hydrogen,

R^7 is





$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $=P(O)R^{11}$,

where

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or a pair of substituents R^{11} and R^{12} or R^{11} and R^{13}, in each case with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and are as defined for R^{11},

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2,

the radicals R^{10} are the same or different and are as defined for R^{11}, R^{12} and R^{13}.

17. A compound as claimed in claim 16, wherein:

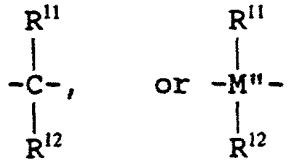
M^1 is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

R^1 and R^2 are identical or different and are methyl or halogen,

R^3 and R^4 are hydrogen,

R^5 and R^6 are identical or different and are methyl, ethyl, or trifluoromethyl,

R^7 is a radical of the formula



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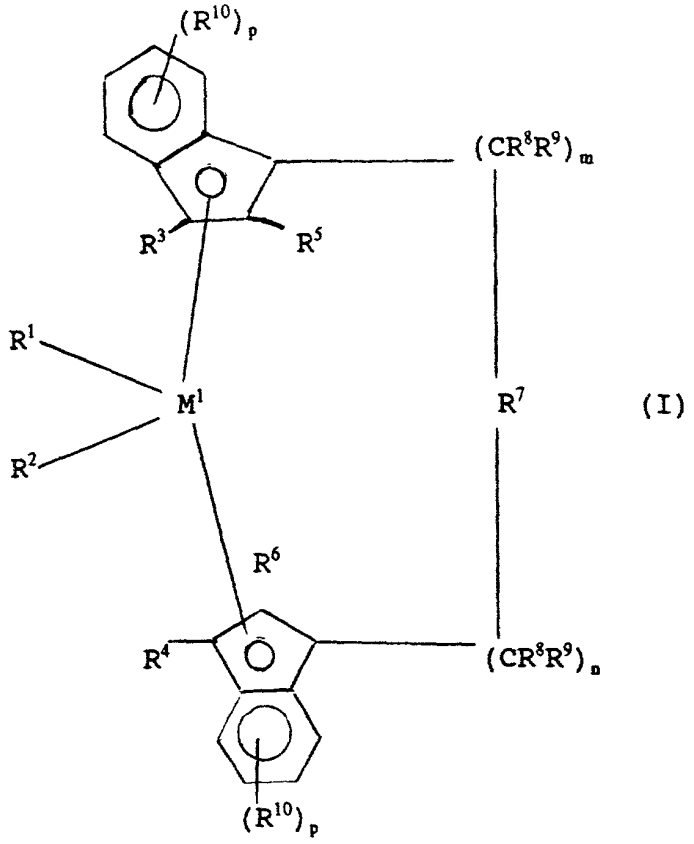
where M" is silicon or germanium, and

R^8 and R^9 are identical or different and are hydrogen or C_1-C_{10}-alkyl.

18. A compound of the formula I



in which

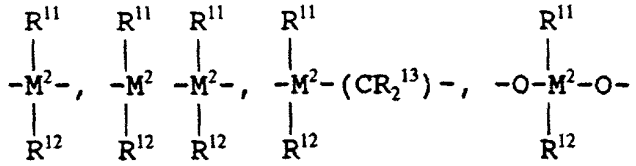
M^1 is a metal from group IVb, Vb or VIb of the Periodic Table,

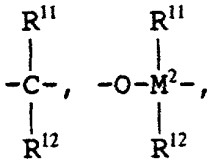
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, which is optionally halogenated, a C_6-C_{10}-aryl group, an $-NR_2^{15}$, $-SR^{15}$, $-OSiR_3^{15}$, $-SiR_3^{15}$ or PR_2^{15} radical in which R^{15} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and are as defined for R^3 and R^4, with the proviso that R^5 and R^6 are not both hydrogen,

R^7 is





$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $=P(O)R^{11}$,

where

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or a pair of substituents R^{11} and R^{12} or R^{11} and R^{13}, in each case with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and are as defined for R^{11},

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2,

p is a number from 1 to 4, and

the radicals R^{10} are the same or different and are a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or a pair of substituents R^{10}, with the atoms connecting them, form a ring.

DECLARATION

I, Andreas Winter, state that I am resident of Taunusblick 10, 61479 Glashütten, Federal Republic of Germany; that I am a citizen of the Federal Republic of Germany; that I am a chemist having graduated at the University of Konstanz, Federal Republic of Germany, with the doctor's degree; that I am acquainted with the subject matter of U.S. Application Ser. No. 08/324,260 filed by Andreas Winter, Jürgen Rohrmann, Martin Antberg, Volker Dolle and Walter Spaleck for METALLOCENES CONTAINING LIGANDS OF 2-SUBSTITUTED INDENYL DERIVATIVES, PROCESS FOR THEIR PREPARATION, AND THEIR USE AS CATALYSTS; that I consider myself qualified by my knowledge of chemistry and specially of the polymerization of olefins by metallocene catalysis and by my 10 years' experience in this field; that I'am an inventor of more than 50 US-patents and patent applications in the field of metallocene catalysis, that I have made the following experiments and observations to wit:

Comparison Example A of US 08/324,260 was repeated with the only difference that, instead of dimethylsilyl(2-methyl-1-indenyl)$_2$ zirconiumdichloride the same amount of dimethylsilyl(3-methyl-1-indenyl)$_2$ zirconiumdichloride was used. The polymer that was obtained had no melting point and n_{iso} = 2,4. This clearly shows that the results obtained in US 08/324,260 are unexpected and superior.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

Frankfurt
this 12th day of February

Andreas Winter

#4

Declaration of Attorney of Record

1. Your declarant, THOMAS M. MESHBESHER, is an attorney of record in the above-identified application and in application Serial No. 08/324,260, the parent of the instant application. Your declarant maintains complete and up-to-date files for the above-identified application and for application Serial No. 08/324,260.

2. Attached to this paper is a true and correct copy of the Assent of Assignee Under 37 CFR 1.172(a), filed in application Serial No. 08/324,260 on March 17, 1995 (in response to a notice of missing parts). Your declarant has reviewed his file of application Serial No. 08/324,260 and can verify, on information and belief, that the said copy of the Assent of Assignee Under 37 CFR 1.172(a) is a true and correct copy of that document.

Your declarant declares further that all statements made herein of his own knowledge are true, and statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under 18 U.S. Code §1001 and that such willful false statements may jeopardize the validity of the above-identified application or any patent issued thereon.

Thomas M. Meshbesher, Reg. No. 25,083

Dec 2, 1997

#4

HOE 90/F 333B
(139*1590)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

ANDREAS WINTER ET AL	:	
REISSUE OF U.S. PAT. 5,276,208	:	Parent Before:
SERIAL NO:	:	ART UNIT: 1505
FILED:	:	EXAMINER: CH 12791 0453 March 12, 155

FOR: METALLOCENES CONTAINING LIGANDS OF: 2-SUBSTITUTED IDENYL DERIVATIVES, PROCESS FOR THEIR PREPARATION AND THEIR USE AS CATALYSTS

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Diane C Pickering
Signature of person mailing paper or

Diane C Pickering
Signature of person making [illegible]

ASSENT OF ASSIGNEE UNDER 37 CFR 1.172(a)

HOECHST AKTIENGESELLSCHAFT, a corporation organized under the laws of the Federal Republic of Germany and having its office and principal place of business at Hoechst Aktiengesellschaft, D-65926 Frankfurt am Main 80, Germany ("the Assignee"), the sole owner of the invention described in U.S. Patent No. 5,276,208, granted on January 4, 1994, assignment recorded in the U.S. Patent and Trademark Office on November 8, 1991 at Reel 5910, Frame 753, hereby assents to the accompanying application to reissue said patent.

The Assignee represents that it has reviewed the required evidentiary records of assignment and hereby certifies that,

to the best of Assignee's knowledge and belief, title is in the Assignee seeking to take the action.

This Assent of Assignee is being executed this 9th day of March, 1995, by two procurists (signatories) or substitutes or nominees of procurists of the Assignee. In the case of execution by a procurist, the signature shall be preceded by the initials "ppa"; in the case of execution by a substitute for or nominee of a procurist, the signature shall be preceded by the initials "iV".

HOECHST AKTIENGESELLSCHAFT

ppa Aulmich
Dr. Aulmich

i V. Schwenk
Dr. Schwenk

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